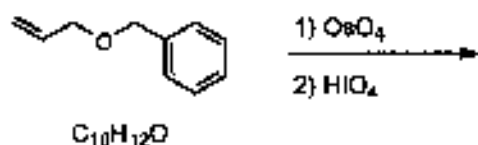


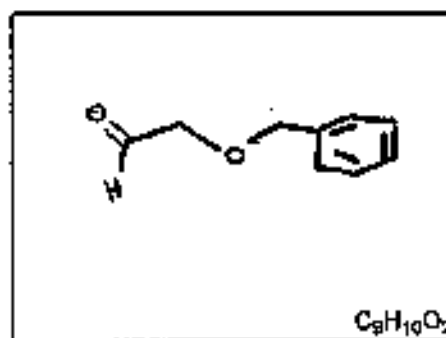
NAME: _____

Final'610B/Pagenkupf

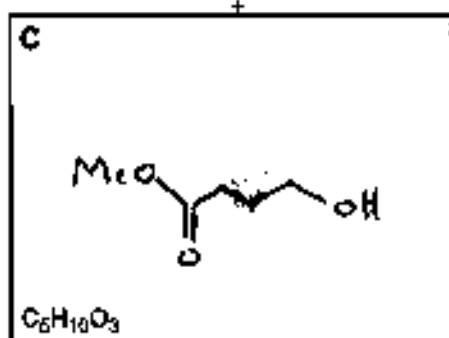
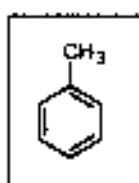
Question 1 (50 points). Roadmap. Provide the products from each reaction in the box. The molecular formula of each product is provided for you. *Clue:* a by-product in the reaction from box B to C is toluene (shown above box C).



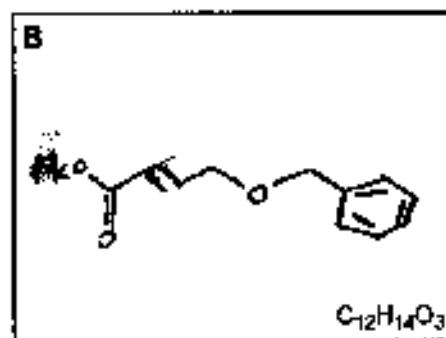
$\text{C}_{10}\text{H}_{12}\text{O}$



$\text{C}_9\text{H}_{10}\text{O}_2$



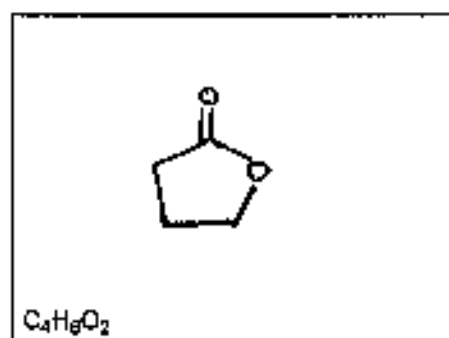
$\text{C}_6\text{H}_{10}\text{O}_3$



$\text{C}_{12}\text{H}_{14}\text{O}_3$

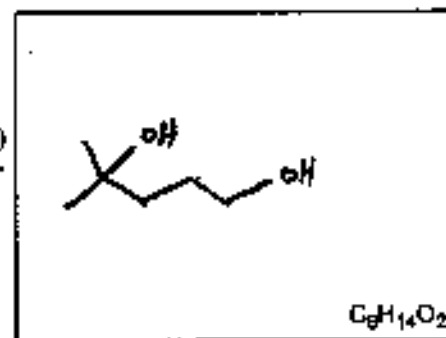
$\text{H}_2, \text{Pd/C}$

$\text{H}^+, \text{mid heat}$



$\text{C}_5\text{H}_8\text{O}_2$

1) MeMgBr (excess)
 2) then work-up

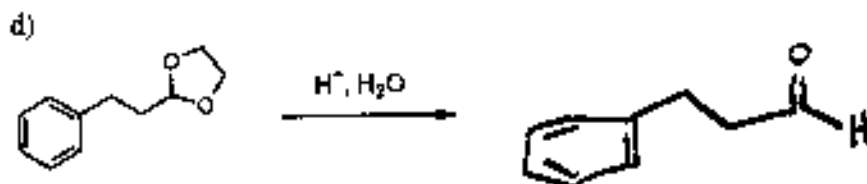
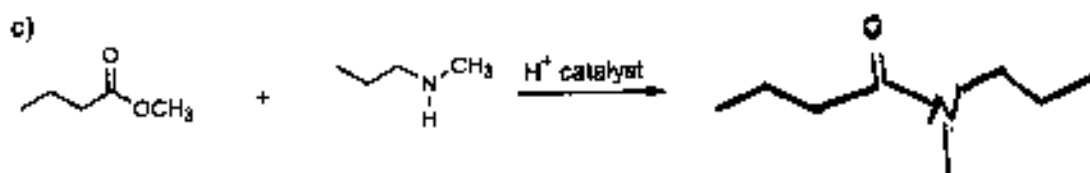
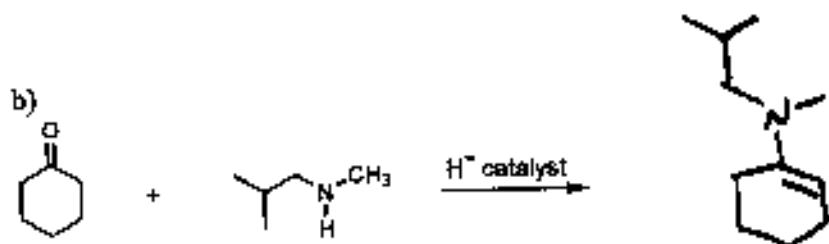
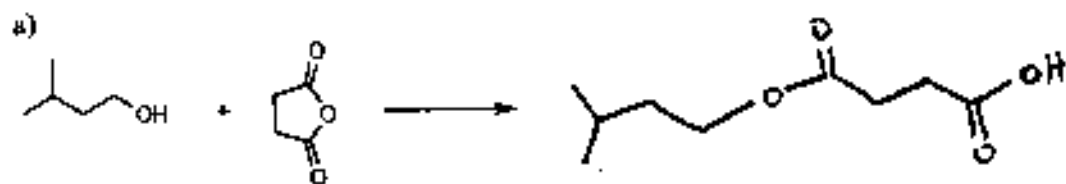


$\text{C}_9\text{H}_{14}\text{O}_2$

NAME: _____

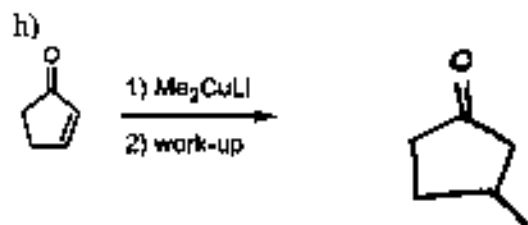
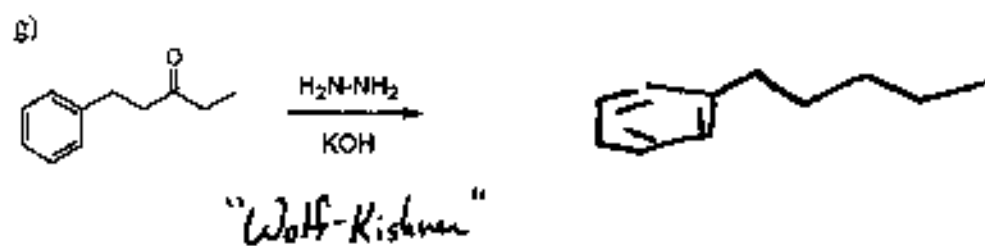
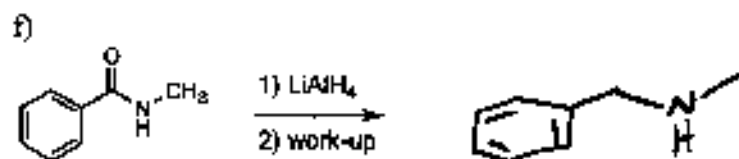
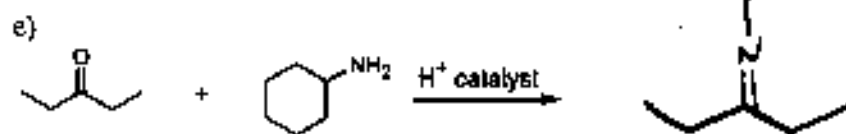
Exam 610B/Pagenkopf

Question 2 (90 points). Reactions. Draw the major product for each of the following reactions.



NAME: _____

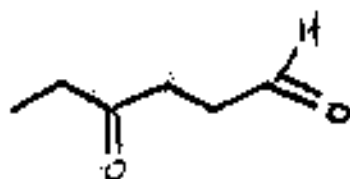
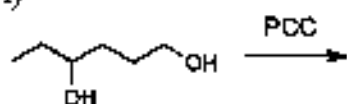
Fidel 6106/Pagethopf



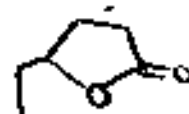
NAME: _____

Final 610B Pagenkopf

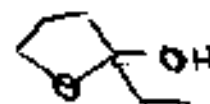
i)



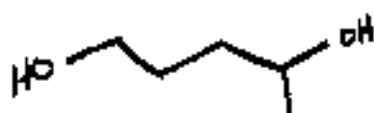
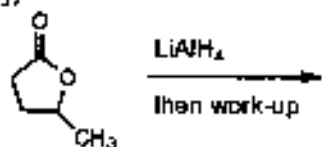
or



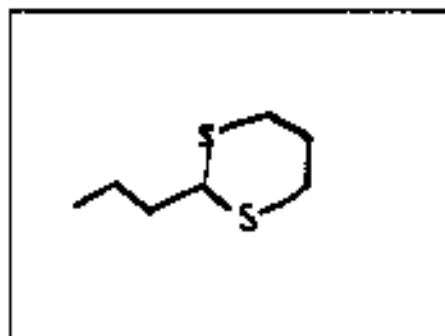
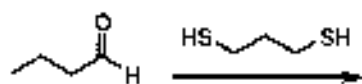
or



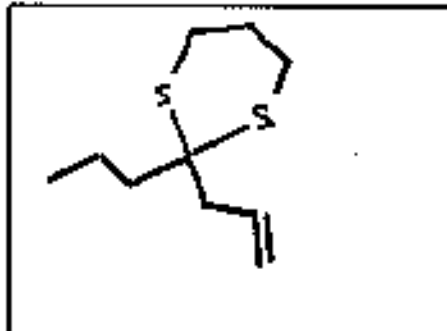
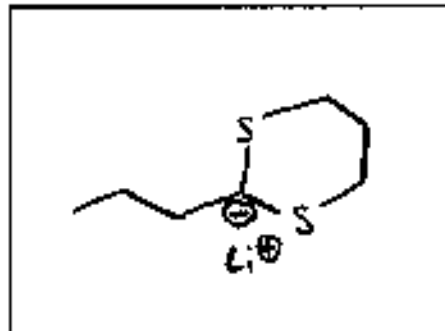
j)



k, l, m)



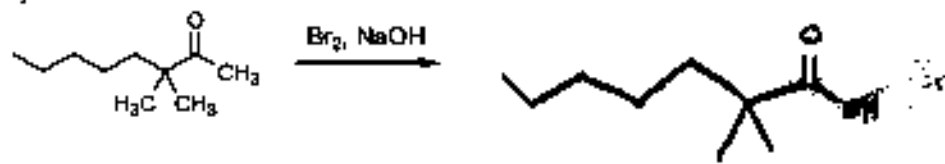
\downarrow n-BuLi



NAME: _____

Final/61.088/Pagenkopf

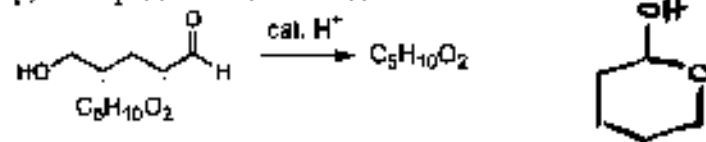
n)



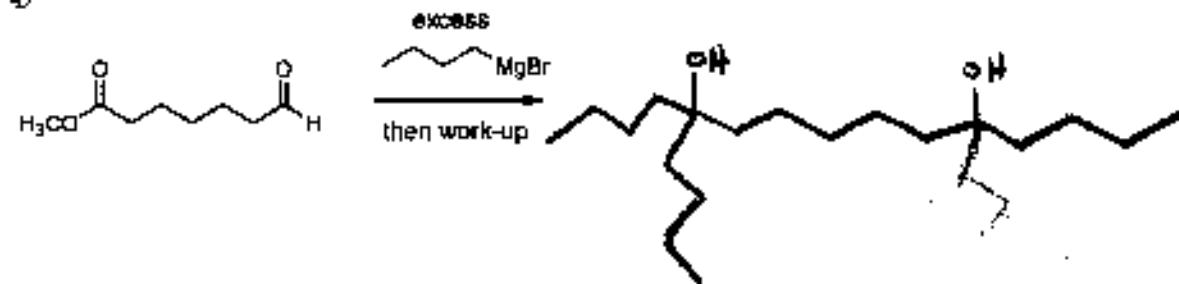
o)



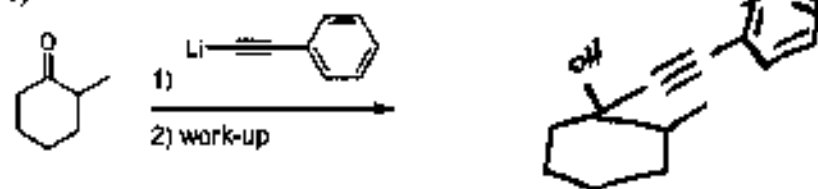
p) hint: product is a hemi-acetal



q)

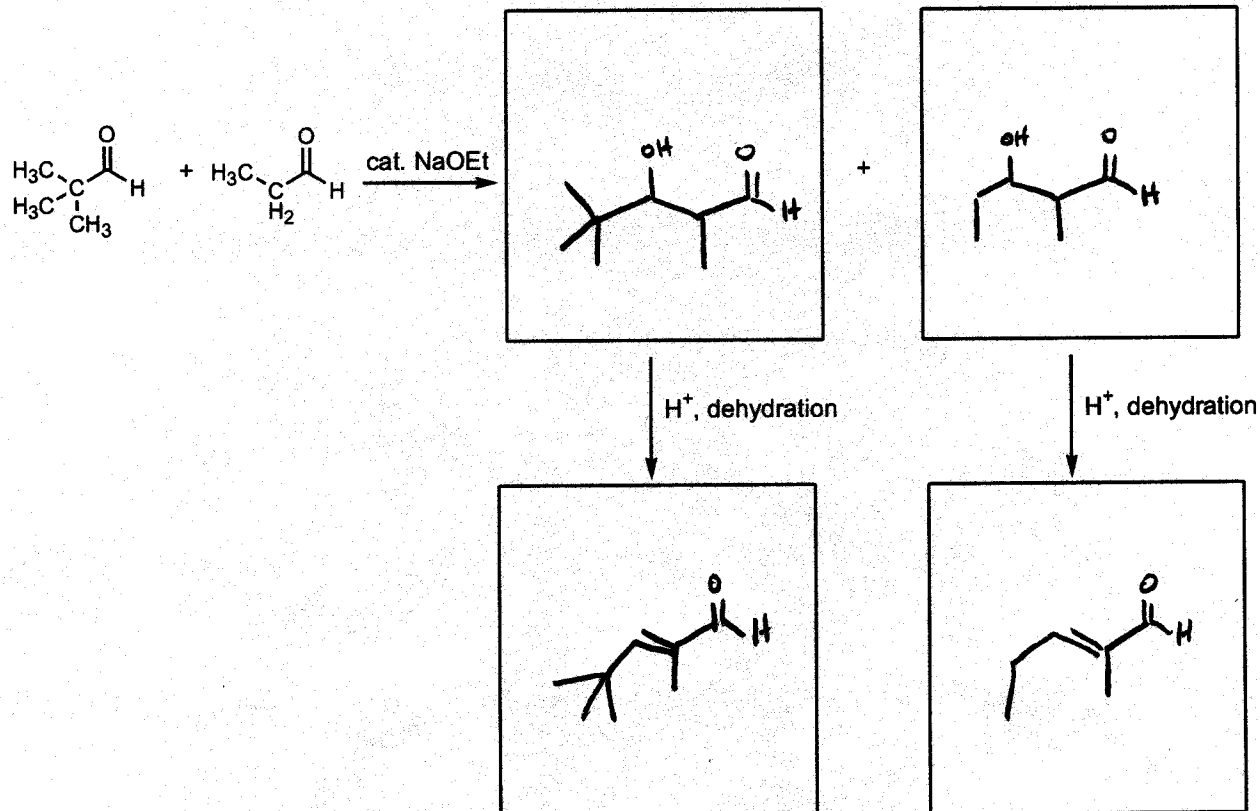


r)



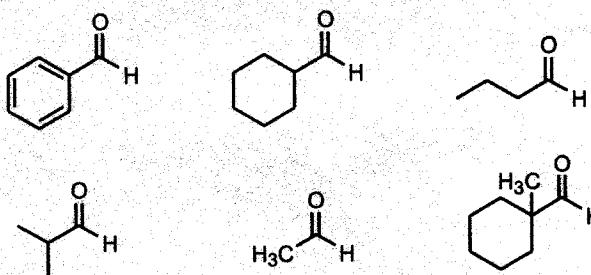
Question 3 (30 points). Aldol Reactions.

a) Show the products of the following aldol condensations. For each question first show one β -hydroxy aldehyde in each of the two boxes, then show the α,β -unsaturated product from dehydration in the next boxes.



b) How many different aldol condensation products (as β -hydroxy aldehydes) are possible from the following mix of aldehydes, even if expected to be a minor product? Circle your answer.

- a) 6
- b) 12
- c) 17
- d) 24**
- e) 28
- f) 35
- g) 36
- h) 128
- i) 46,656

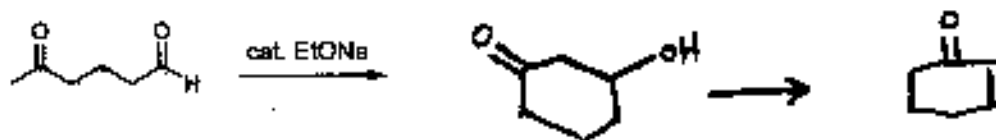


Nucleophiles - 4
 Electrophiles - 6

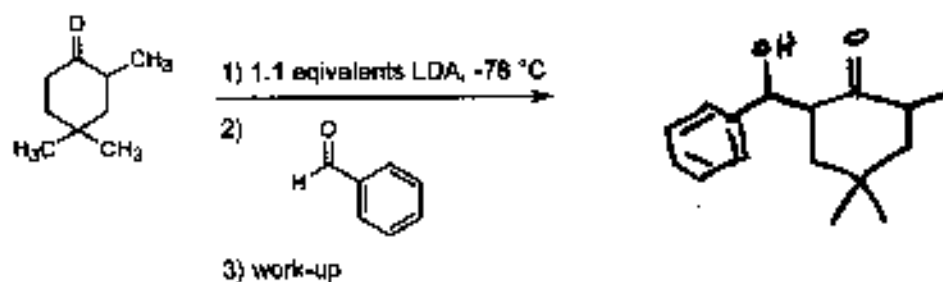
 24

Aldol Reactions continued.

c) (20 points) The following molecule undergoes a self (or intramolecular) aldol condensation followed by elimination (or dehydration) when treated with catalytic EtONa. Show the intramolecular aldol product after dehydration.

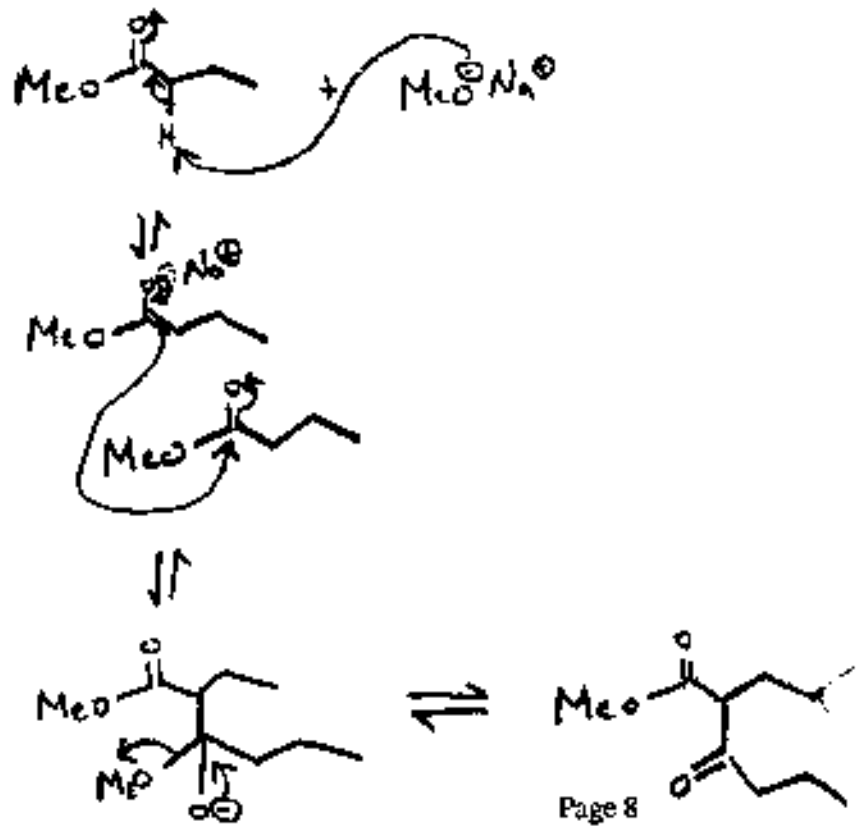
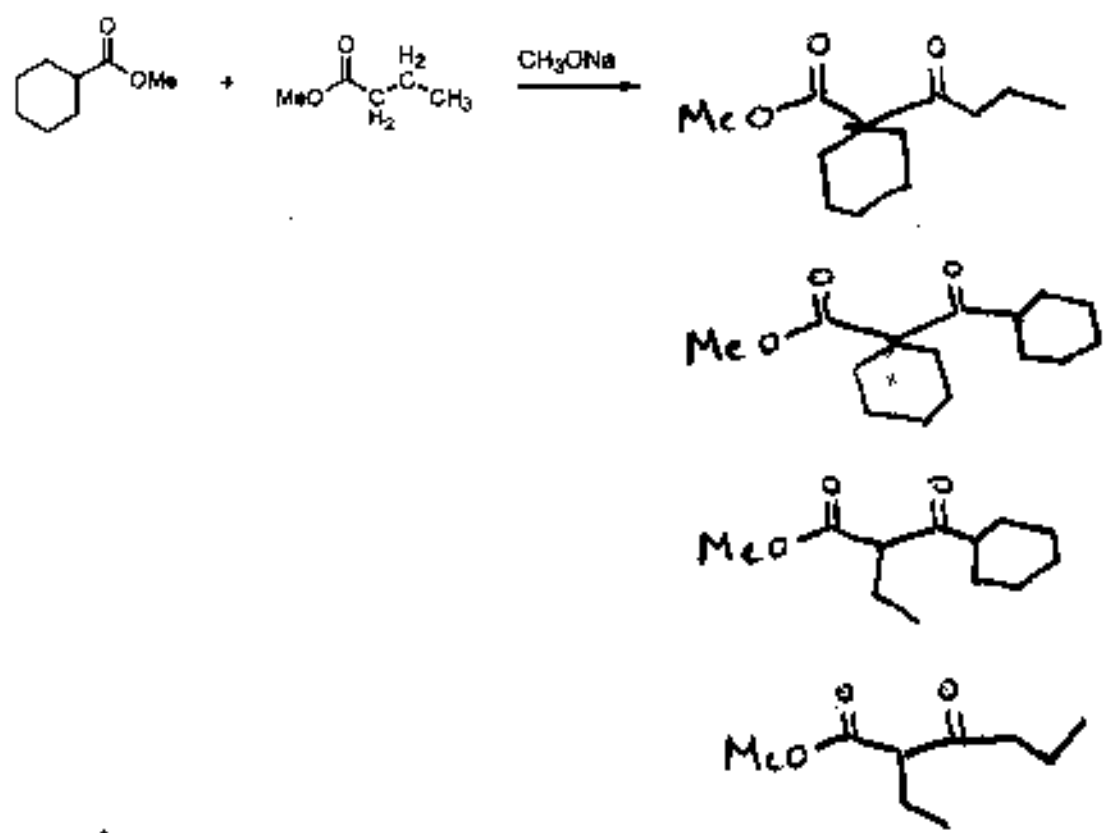


d) (10 points) What is the major aldol product formed under the conditions indicated? You may assume that the ketone only reacts with benzaldehyde and not itself. *reminder*: LDA = LiN(CH₂CH₃)₂

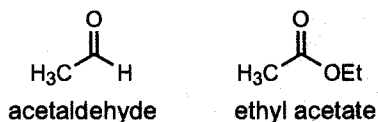


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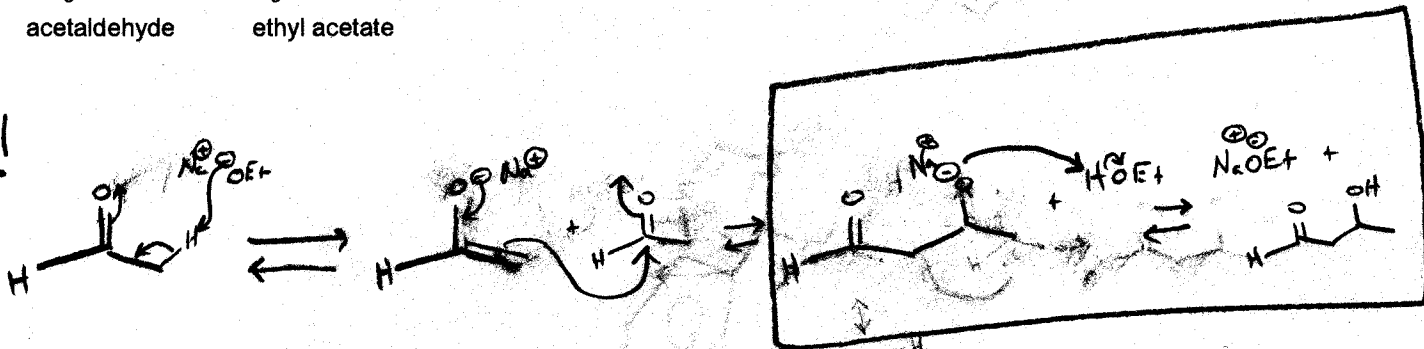
Question 4 (35 points). Claisen Condensations. Show the four products from the following Claisen condensation. Also, show a detailed mechanism for the formation of one of the four products.



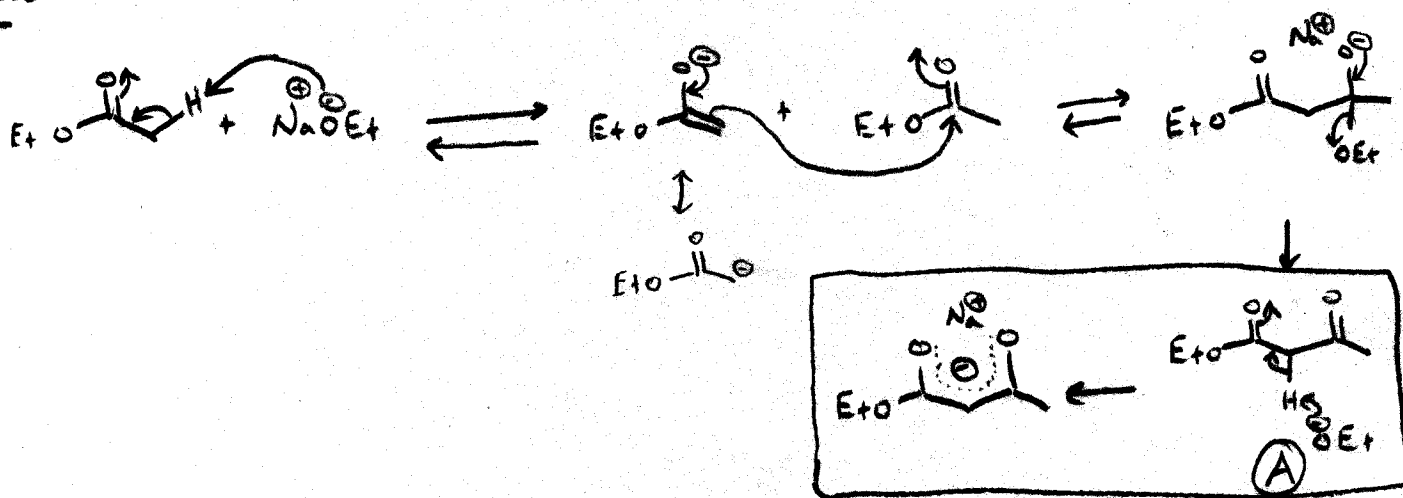
Question 5 (20 points). Brief Essay. Explain why an aldol reaction needs only catalytic amounts of EtONa but a Claisen reaction (typically) requires a full equivalent. Your explanation must use specific chemical structures and address the relative acid and base strengths of starting materials, intermediates and products. Show structures and comment on the stabilities of the enolates involved, equilibrium in the reactions and on mechanisms. However, the emphasis should be on relative acid/base strengths and equilibrium (show the equilibrium equations), but specific pKa's are not necessary. To illustrate your answer, use acetaldehyde for the aldol and ethyl acetate for the Claisen.



Aldol



Claisen



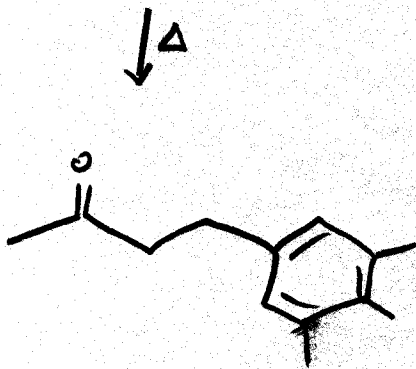
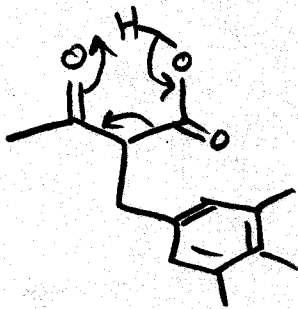
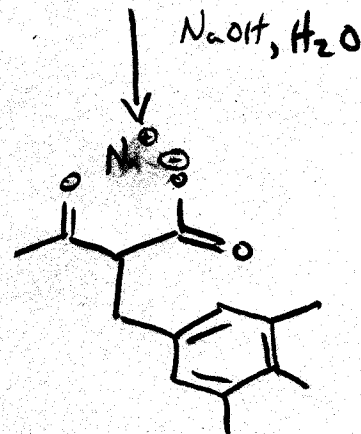
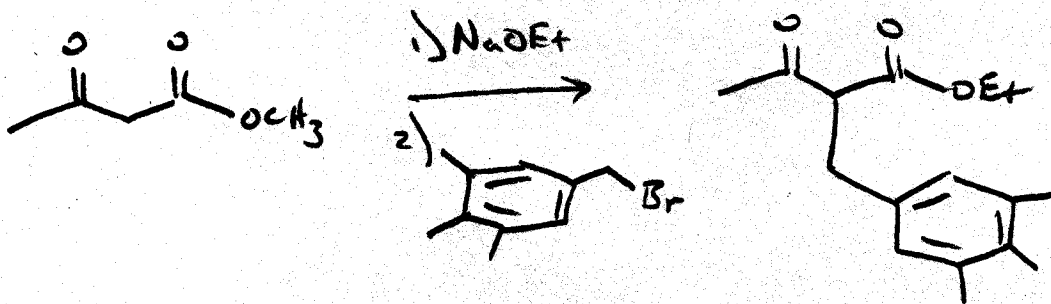
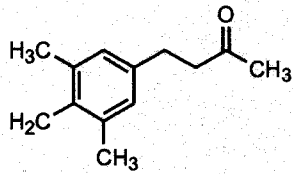
The aldol reaction has a hydrogen α to the carbonyl with a $pK_a = 23$. The product has a alcohol with a $pK_a = 16$. The HOEt is in equilibrium with the alkoxide to give Na^+OEt^- and the product.

The Claisen rxn has an α -hydrogen with $pK_a = 23$. Intermediate **A** has a proton with a $pK_a = 7-8$.

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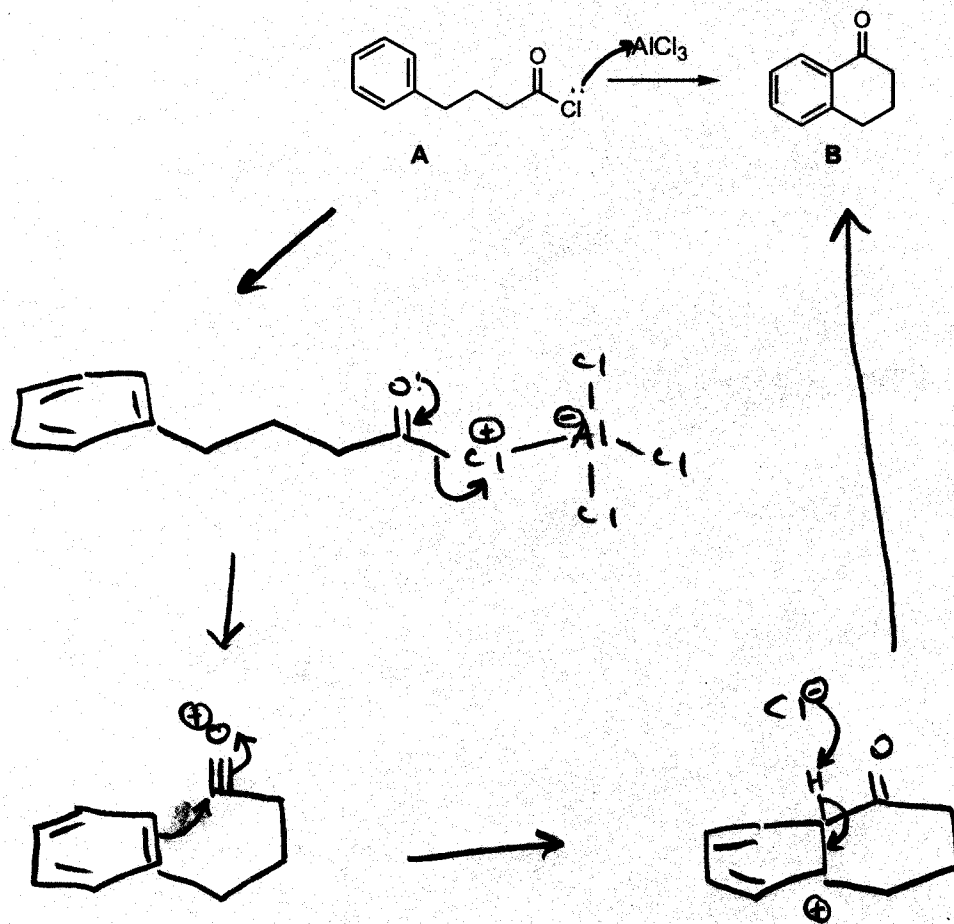
Question 6 (20 points). Show how to synthesize the following compound using either the malonic ester synthesis or the acetoacetic ester synthesis by providing the necessary reagents and conditions.



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Question 7 (15 points). Mechanisms. When **A** is treated with aluminum trichloride, **B** is formed in high yield. Propose a mechanism for this transformation.

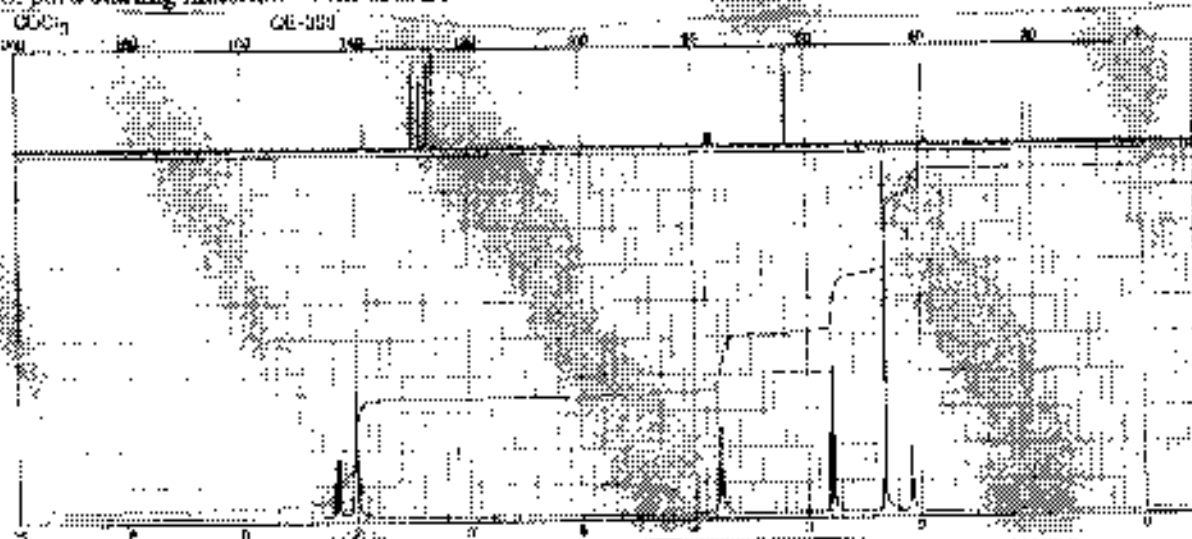


NAME: _____

Acad. Period: _____

Question 8. NMR.

a) 5 points. A student was asked to make a Grignard reagent from *para*-bromotoluene and then treat this with ethylene oxide. When the student was almost finished, he noticed that there were two bottles of starting material, one labeled *meta* and the other labeled *para*. However, he didn't know which bottle he had used! The student started to panic, but you told him not to worry because you could help. After looking at the NMR of his reaction product (shown below) do you think he used the *meta* bottle of *para* starting material? YES or NO?



PERIODIC TABLE OF THE ELEMENTS

Atomic numbers and names based on IUPAC nomenclature. In parentheses are the most stable isotopes.

Periods																Groups														
1	2											13A	14A	15A	16A	17A	18A													
1	H											B	C	N	O	F	Ne													
2	Li	Be											Al	Si	P	S	Cl	Ar												
3	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Au	Hg
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
7	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr													

Lanthanide series:

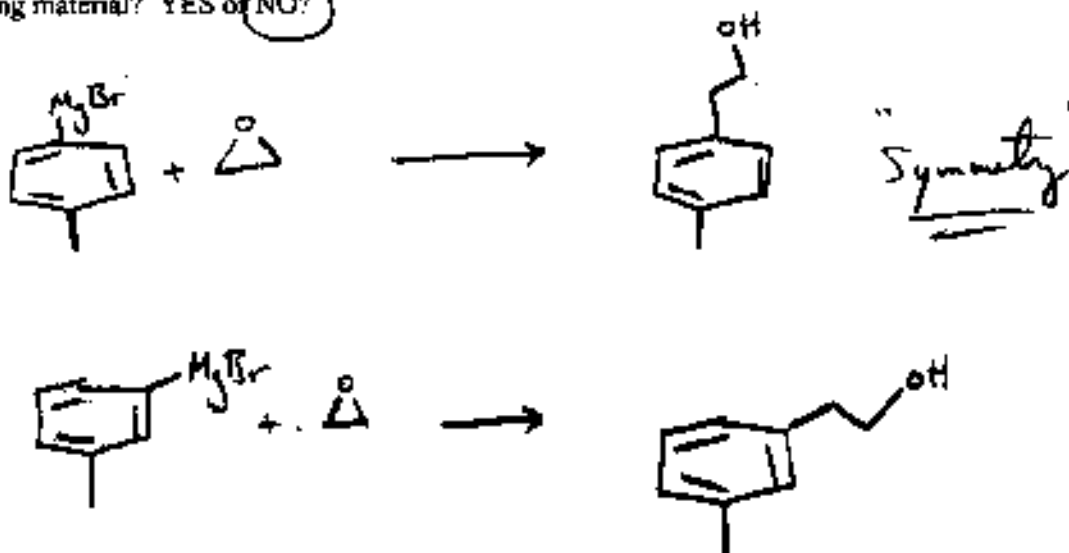
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Actinide series:

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Question 8. NMR.

a) 5 points. A student was asked to make a Grignard reagent from *para*-bromotoluene and then treat this with ethylene oxide. When the student was almost finished, he noticed that there were two bottles of starting material, one labeled *meta* and the other labeled *para*. However, he didn't know which bottle he had used! The student started to panic, but you told him not to worry because you could help. After looking at the NMR of his reaction product (shown below) do you think he used the correct bottle of *para* starting material? YES or NO?



PERIODIC TABLE OF THE ELEMENTS

Atomic masses are based on ¹²C. Atomic masses in parentheses are for the most stable isotopes.

B Atomic number C Symbol 12.011 Atomic mass																		VIIA He 4.00260																	
IA H 1.00794												IVA B 10.81		VA C 12.011		VIA N 14.0064		VIIA O 15.9994		VIII F 18.9984		IX Ne 20.179													
II A Li 6.941		III A Be 9.01218												IVA Al 26.9815		VA Si 28.0855		VIA P 30.97376		VIIA S 32.06		VIII Cl 35.453		IX Ar 39.948											
III B Na 22.98976		IV B Mg 24.305		V B Sc 44.9559		VI B Ti 47.88		VII B V 50.9415		VIII B Cr 51.996		IX B Mn 54.9380		X B Fe 55.847		XI B Co 58.9332		XII B Ni 58.71		I Cu 63.546		II Zn 65.38		III Ga 69.72		IV Ge 72.64		V As 74.9216		VI Se 78.96		VII Br 79.904		VIII Kr 83.80	
IX K 39.0983		X Ca 40.078		XI Sc 44.9559		XII Ti 47.88		XIII V 50.9415		XIV Cr 51.996		XV Mn 54.9380		XVI Fe 55.847		XVII Co 58.9332		XVIII Ni 58.71		XIX Cu 63.546		XX Zn 65.38		XXI Ga 69.72		XXII Ge 72.64		XXIII As 74.9216		XXIV Se 78.96		XXV Br 79.904		XXVI Kr 83.80	
XXVII Rb 85.4678		XXVIII Sr 87.62		XXIX Y 88.906		XXX Zr 91.224		XXXI Nb 92.9064		XXXII Mo 95.94		XXXIII Tc 98		XXXIV Ru 101.07		XXXV Rh 106.905		XXXVI Pd 106.4		XXXVII Ag 107.868		XXXVIII Cd 112.411		XXXIX In 114.818		XL Sn 118.710		XLI Sb 121.757		XLII Te 127.6		XLIII I 126.905		XLIV Xe 131.29	
XLV Cs 132.905		XLVI Ba 137.33		XLVII La 138.905		XLVIII Hf 178.49		XLIX Ta 180.947		L W 183.85		LI Re 186.207		LII Os 190.2		LIII Ir 192.22		LIV Pt 195.08		LV Au 196.967		LVI Hg 200.59		LVII Tl 204.37		LVIII Pb 207.2		LIX Bi 208.98		LX Po 209		LXI At 210		LXII Rn 222	
LXIII Fr [223]		LXIV Ra [226]		LXV Ac [227]		LXVI Unq [285]		LXVII Unp [285]		LXVIII Unh [285]																									

*Lanthanide series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.907	144.24	[145]	150.4	151.96	157.25	158.9254	162.50	164.9303	167.26	168.934	173.04	174.967

†Actinide series

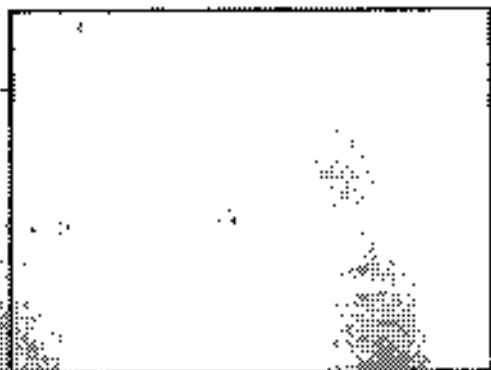
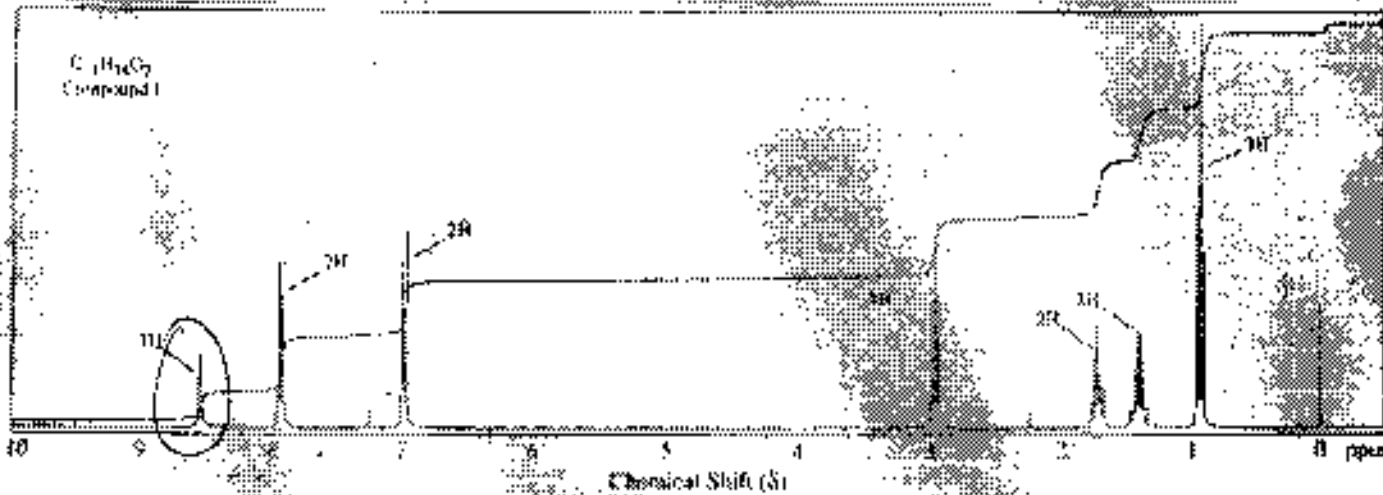
88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
232.037	231.036	238.0289	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]	[260]		

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NMR Continued.

h) 15 points. Compound I, $C_{11}H_{14}O_2$, is insoluble in water, aqueous acid, and aqueous $NaHCO_3$, but dissolves readily in 10% Na_2CO_3 and 10% $NaOH$. When these alkaline solutions are acidified with 10% HCl , compound I is recovered unchanged. Given this information and its 1H -NMR spectrum, deduce the structure of compound I and draw your structure in the box at the bottom of this page.



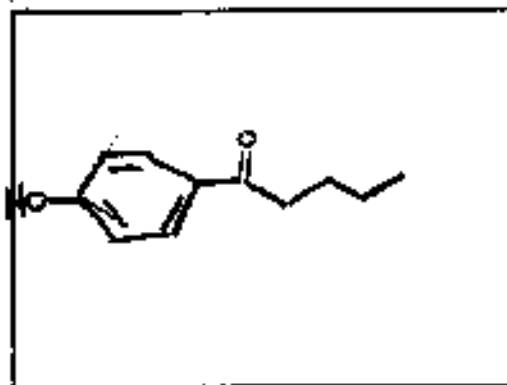
NMR. Continued.

b) 15 points. Compound I, $C_{11}H_{14}O_2$, is insoluble in water, aqueous acid, and aqueous $NaHCO_3$ but dissolves readily in 10% Na_2CO_3 and 10% $NaOH$. When these alkaline solutions are acidified with 10% HCl , compound I is recovered unchanged. Given this information and its 1H -NMR spectrum, deduce the structure of compound I and draw your structure in the box at the bottom of this page.

8.5 ppm	1H		
7.9 ppm	2H	d	
7.0 ppm	2H	d	
3.0	2H	t	$X-CH_2-CH_2$
1.6	2H	m	$-CH_2-$
1.4	2H	m	$-CH_2-$
0.9	3H	t	CH_3-CH_2

Soluble in 10% $NaOH$

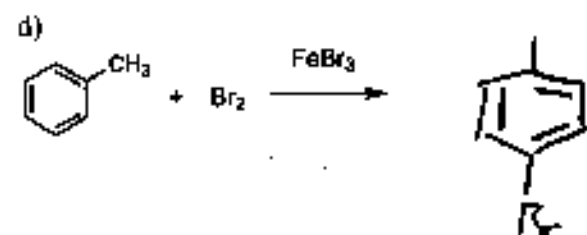
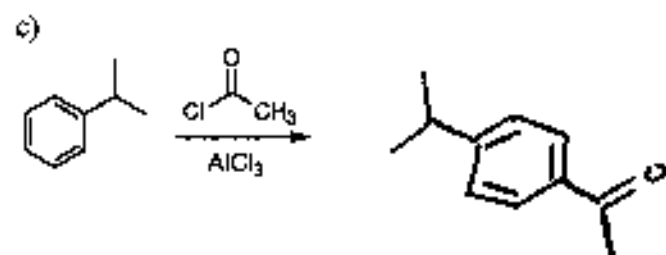
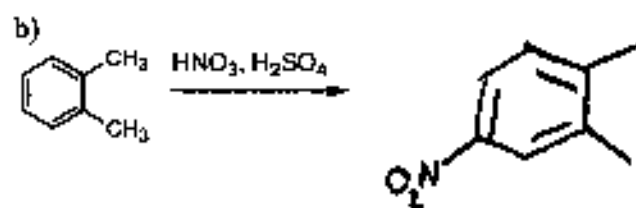
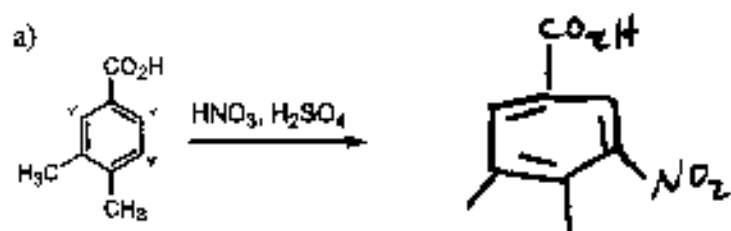
Not Soluble in $NaHCO_3$



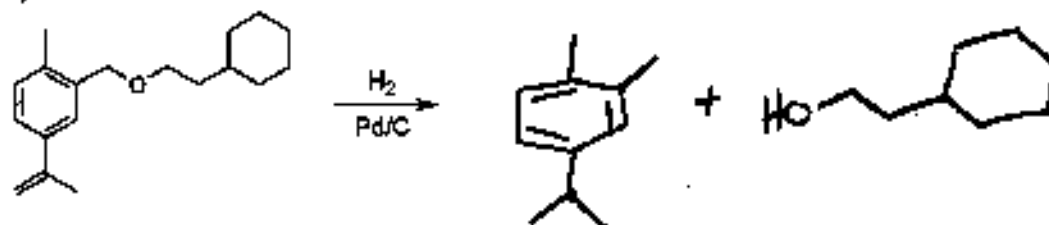
NAME: _____

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Question 9 (30 points). Electrophilic aromatic substitution reactions. Draw the major product expected from each of the following reactions. For each nitration reaction, add only one nitro group to the aromatic ring.



e) Two Products



Question 10 (40 points). Synthesis. DEET, *N,N*-diethyl-*m*-toluamide, is the active ingredient in several common insect repellents. Propose a synthesis of DEET from benzene. There are numerous viable synthetic routes to DEET and it may help to think about the problem retrosynthetically. For example, if the last transformation(s) you propose is preparation of the amide from another carboxylic acid derivative, then the problem may simplify considerably. With two functional groups that we know how to attach to benzene, all we need to do is select a sequence that ensures their *meta* relationship.

